En route towards panchromatic light harvesting: photophysical and electrochemical properties of Bodipy–porphyrazine conjugates†

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The concept of panchromatic light harvesting, that is, broad absorption cross sections throughout most of the visible range and excited state funnelling, has been realized in a novel set of porphyrazines. On one hand, zinc, copper, or magnesium ions were complexed by porphyrazines to tune their ground and excited state features. On the other hand, up to eight Bodipys were covalently attached to the periphery of the porphyrazines to enhance the ground state absorption. The corresponding star-shaped conjugates were probed by advanced photophysical measurements, that is, time-resolved fluorescence and femtosecond transient absorption spectroscopy. From the latter we derive spectroscopic and kinetic evidence in support of a fast and unidirectional energy transfer from the photoexcited Bodipy at the periphery to the porphyrazine at the core. In addition, the impact of the different metal centers is demonstrated.

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Introduction

During recent decades, mimicking the photochemical process of natural photosynthesis by means of bio-inspired synthetic models has become a mature field.¹ Converting sunlight into energy and the development of molecular systems that mimic photosynthesis are a key step, but also impact the construction of optoelectronic devices like dye-sensitized solar cells as well as more general photonics and photo-catalysis applications.² The need to integrate light harvesting, energy transfer, charge transfer, charge transport, and catalysis processes into a single system renders artificial photosynthesis complex.³ In this context, organic chromophores based on tetrapyrrolic systems like porphyrins or phthalocyanines have been widely employed as light capturing antenna systems and/or electron donors.^{4–8}

Substitutions of tetraaza pyrrolic systems, especially in the β -positions of their pyrrolic subunits, induces characteristic changes with respect to their strong absorptions at both ends of the visible spectrum, their redox potentials, and their photochemical stability. Any of the aforementioned would render, for example, phthalocyanines promising building blocks for photoactive materials that are applicable in solar energy

conversion.⁹ Notably, phthalocyanines, or more generally, porphyrazines, are usually built up with a low degree of synthetic flexibility as substituents have to be implemented at the precursor stages.^{9,10} Peripheral annulations of the porphyrazine core have a marked impact on the overall aromaticity of the macrocycle.¹¹ As a matter of fact, the electronic and optical properties change.^{12,13} However, in porphyrazines only a rather moderate absorption cross section evolves between the high-energy B-band and the low-energy Q-band in the 430 to 700 nm region.¹⁴

Apart from tetraaza pyrrolic macrocycles, boron dipyrins (Bodipys) are also of particular interest, especially in the context of light harvesting and energy transfer. Bodipys are well known for their high extinction coefficients, high fluorescence quantum yields, long lived excited states, suitable excited state energies, excellent photostability, and stability in many solvents.¹⁵

Additionally, the modification of Bodipy is a versatile approach to tailor the absorption/emission properties throughout the 450–680 nm range and to optimize the energy/electron donor features.^{16–18} In a few studies, energy transfer between Bodipy and coordinatively linked porphyrins, perylenediimides or subphthalocyanines has been demonstrated.^{16,19,21} Additionally there are some reports with Bodipy porphyrin/phthalocyanine conjugates covalently linked.^{1,20,22–24}

We recently reported on the synthesis and photophysical investigation of a zinc-containing dibenzoquinaxalino porphyrazine with eight covalently attached Bodipy units (1-/2-Zn).²⁴ This multi-chromophore light harvesting system reveals efficient intramolecular energy transfer from the photoexcited Bodipy to the porphyrazine and, in addition, shows an efficient

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intermolecular electron transfer from a pyridyl-functionalized phenothiazine coordinated to the photoexcited porphyrazine.²³ In this paper we focus on the impact of the divalent metal ions in the porphyrazine center on the photophysical properties of the light harvesting system. We describe the preparation of the Bodipy–porphyrazine conjugates **1** and **2** with complexed Mg, Zn or Cu ions in the porphyrazine cavity (Chart 1) and discuss their photophysical and electrochemical features as determined by time-resolved fluorescence and femtosecond transient absorption spectroscopy as well as by cyclovoltammetry and spectroelectrochemical methods.

Results and discussion

Synthesis

The preparation of Bodipy–porphyrazine conjugates **1** and **2** follows routes closely related to those previously published – shown in Scheme 1.²⁴ Central to the synthesis is compound **3**, a versatile building block for highly functionalized porphyrazines. Demetallation of **3-Mg** using *p*-toluene sulfonic acid²⁴ and the subsequent addition of the corresponding metal acetate lead to **3-Zn** (ref. 24) and **3-Cu**, respectively. The Bodipy-functionalized alkynes **5** (ref. 25) and **7** (ref. 24) (Chart 2) were connected to porphyrazines **3** (Mg, Zn, and Cu) using modified Hagihara–Sonogashira conditions in respectable yields of up to 72% for **1-Cu/2-Cu**. The preparation of **1-Zn/2-Zn**²⁴ and **1-Mg/2-Mg** posed a significant challenge, as the co-catalyst CuI, commonly used in Hagihara–Sonogashira coupling reactions, was strictly avoided to prevent partial metal ion exchange. Hence the yield of the Zn/Mg-congeners of **1** and **2** is somewhat lower than that of the corresponding Cu-porphyrazines.

Chart 1 Bodipy–porphyrazine conjugates **1-Zn**, **2-Zn**, **1-Mg**, **2-Mg**, **1-Cu**, and **2-Cu**.

Reference compound **4** (Chart 2) either as a free base **4-H₂** or with complexed Cu, Mg, or Zn metal ions could be synthesized along a similar route – see the ESI.†

The formation of the sixteen fold alkynylated porphyrazines **1–4** was verified *via* MALDI mass spectrometry and NMR-spectroscopy – see the ESI.†²⁴ Difficulties were observed with **2-Mg**, for which we were unable to obtain a clear molecular ion signal in the MALDI mass spectrum. However, the constitution of **2-Mg** was ascertained by NMR-spectroscopy, which featured characteristic porphyrazine and Bodipy signals in the respective ¹H and ¹⁹F-NMR-spectra. The absorption spectra give additional evidence for the structures of Bodipy–porphyrazine conjugates **1** and **2** as they consist of superimposable absorption features – see Fig. 3, S7, and S8† and Table 2.

Free-base porphyrazine

Recent work has documented that the behavior of free-base porphyrazines upon protonation is easily followed by steady-

Chart 2 Molecular structures of model compounds **4** to **7**.

state absorption spectroscopy.^{26,27} In particular, changes in the absorption spectrum, especially with respect to shape and position of the long-wavelength Q-band, seem to correlate with the solvent polarity and the protonation of the chromophore. Overall, the electronic transitions are red-shifted and the Q-band is split into two due to the transformation of D_{4h} symmetry into D_{2h} symmetry.²⁶ Dissolving, for example, the free-base porphyrazine **4-H₂** in toluene gives rise to a broad absorption with a Soret-band at 410 nm and two Q-band maxima at 713 and 737 nm resulting from the D_{2h} symmetry. In titration experiments of **4-H₂** with trifluoroacetic acid the two maxima merge into a single broad band at 721 nm – see Fig. 1 (top). This leads to the assumption of the protonation of all of the azomethine nitrogens in **4-H₂**.²⁶ Qualitatively, this behavior is reversible: Fig. 1 (bottom) documents a titration experiment of protonated **4-H₂** with triethylamine, leading to

the stepwise disappearance of the maximum at 737 nm, which eventually merges into a single band at 703 nm. This strongly corroborates the impact of protonation on free-base porphyrazine.²⁸

Metalloporphyrazines

Electrochemical characterization. The electrochemical properties of **1**, **2**, **4**, **5**, and **6** were investigated by cyclic and square wave voltammetry. The data are reported vs. ferrocene/ferrocenium (Fc/Fc^+) and are summarized in Table 1. Analyses of the cyclic voltammograms of **4-Mg**, **4-Zn**, and **4-Cu** reveal reversible processes in the reduction range at -0.99 V (**4-Mg**), -0.96 V (**4-Zn**), and -0.98 V (**4-Cu**). A comparison of all three is shown in Fig. 2. Turning to **5** and **6**, reversible processes are discernable in the reduction range at -1.55 V for **5** as well as at -0.99 V for **6**. The cyclic voltammograms of **1-Mg** and **2-Mg**, which bear covalently linked Bodipys, are shown in Fig. S1.† Overall, the reduction potentials are shifted towards higher potentials relative to **4-Mg** (-0.97 V) as well as lower potentials, namely -1.33 V, relative to **5**. We note that the Bodipy reduction overlaps with the porphyrazine reduction and, therefore, a more detailed analysis is rather difficult. Similar changes occur in **1-Zn** and **2-Zn**, which are illustrated in Fig. S2.† In the reduction range, the potentials for **4-Zn** are shifted towards lower potentials. The reduction of **1-Cu** is affected in the same manner with a reduction of porphyrazine at -0.935 V and of Bodipy at -1.31 V – see Fig. S3.†

Photophysical characterization. The steady-state absorption spectra of **4-Mg** feature a characteristically broad spectrum in the UV-visible region, which reaches out to the Q-band at $\lambda_{\text{max}} = 707$ nm. Changing the metal to either **4-Zn** or **4-Cu** leads to no appreciable changes at first glance – see Fig. S4.† A closer look at the Q-band reveals, however, slight shifts of about 4 nm for **4-Zn** ($\lambda_{\text{max}} = 703$ nm) and about 3 nm for **4-Cu** ($\lambda_{\text{max}} = 704$ nm). Table 2 summarizes all of the steady-state absorption data. Please note that when dissolving porphyrazines in coordinating solvents such as THF, strong red shifts up to about 10 nm are observed. Fig. S5† summarizes the spectra of **4-Mg** in different solvents.

Fig. 1 Absorption spectra of free base porphyrazine **4-H₂** in toluene at room temperature. Top: titration experiments with successive addition of trifluoroacetic acid (from 0 to 1000 μL) – insert: zoomed in view of the Q-bands illustrating the red-shift and the increase of the Q-band absorptions at 737 nm. Bottom: titration experiments with successive addition of triethylamine (from 0 to 1000 μL) – insert: zoomed in view of the Q-bands illustrating the blue shift and the decrease of the Q-bands at 737 nm.

Table 1 Redox potentials in the reduction range of **5**, **6** and the corresponding **4**, **1**, and **2** vs. Fc/Fc^+ (0.2 V) in toluene–acetonitrile (4 : 1 v/v) with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte

	$E_{1/2}$ porphyrazine	$E_{1/2}$ Bodipy
5		-1.545
6		-0.945
4-Zn	-0.96	
1-Zn	-0.81	-1.41
2-Zn	-0.65	-1.14
4-Mg	-0.985	
1-Mg	-0.97	-1.33
2-Mg	-0.975	—
4-Cu	-0.97	
1-Cu	-0.935	-1.31
2-Cu	-0.945	—

Fig. 2 Cyclic voltammograms of 4-Cu (black), 4-Mg (red), and 4-Zn (grey), measured at room temperature in degassed toluene–acetonitrile (4 : 1 v/v) with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte.

Fig. 3 Absorption spectra in the visible region of 5 (blue), 6 (dark cyan), 4-Mg (black), 1-Mg (red), and 2-Mg (grey) in toluene at room temperature.

Table 2 Summary of steady-state spectroscopic data of porphyrazines 1, 2 and 4, and Bodipys 5 and 6 measured in toluene

	Absorption		Fluorescence		
	$\lambda_{\text{max}}/\text{nm}$	$(\epsilon/\text{mol}^{-1} \text{cm}^{-1})$	$\lambda_{\text{max}}/\text{nm}$	ϕ	τ/ns
$\lambda_{\text{ex}} = 680 \text{ nm}$					
4-Zn	703	(136 192)	710	0.2	1.92
1-Zn	706	(111 960)	710	0.12	1.91
2-Zn	706	(111 307)	710	0.08	1.27
4-Mg	707	(147 013)	710	0.19	4.95
1-Mg	707	(64 100)	710	0.06	5.26
2-Mg	707	(95 947)	710	0.013	5.73
4-Cu	704	(238 240)	—	—	—
1-Cu	711	(114 078)	—	—	—
2-Cu	711	(68 095)	—	—	—
$\lambda_{\text{ex}} = 520 \text{ nm}$					
5	528	(86 929)	550	0.69	5.39
1-Zn	528	(335 827)	550	0.091	—
1-Zn	—	—	710	0.019	—
1-Mg	528	(316 158)	550	0.044	—
1-Mg	—	—	710	0.008	—
1-Cu	528	(510 565)	550	0.026	—
1-Cu	—	—	710	—	—
$\lambda_{\text{ex}} = 560 \text{ nm}$					
6	580	(65 913)	600	0.54	3.74
2-Zn	580	(342 248)	600	0.098	4.03
2-Zn	—	—	710	0.021	—
2-Mg	580	(330 977)	600	0.038	3.78
2-Mg	—	—	710	0.025	—
2-Cu	580	(200 782)	600	0.015	3.15
2-Cu	—	—	710	—	—
$\lambda_{\text{ex}} = 410 \text{ nm}$					
4-Zn	703	(136 192)	475	0.058	—
4-Mg	707	(147 013)	475	0.008	—
4-Cu	704	(238 240)	480	0.002	—

The characteristic steady-state absorption features of 5 and 6 are derived from Fig. S6,† with weak absorptions in the UV region and strong absorption maxima at 528 and 580 nm. The absorptions of 1-Mg and 2-Mg are depicted in Fig. 3. The visible region is dominated by a broad absorption stemming from the porphyrazine followed by the characteristic features of the corresponding Bodipy, before the Q-band of the porphyrazine sets in. 1-Zn and 2-Zn show the same features, with the only exception that the Q-band maximum appears at 703 nm – see Fig. S7.† Examples for 1-Cu and 2-Cu are shown in Fig. S8† and they, too, resemble those of the individual constituents. With these data in hand, it is safe to assume that interactions between Bodipy substituents and porphyrazine in the ground state are negligible.

In parallel, the excited state properties were derived from fluorescence measurements. Table 2 summarizes the excited state properties. When exciting the Soret-band of 4 at 410 nm, a rather strong second singlet excited state fluorescence, namely S2, with 475 nm maxima for 4-Mg and 4-Zn and a 480 nm maximum for 4-Cu is observed – see Fig. S9.† For these, fluorescence quantum yields of 0.008 (4-Mg), 0.058 (4-Zn), and 0.002 (4-Cu) were calculated. Furthermore, strong S1 fluorescence is detected at 710 nm for 4-Zn and 4-Mg. In contrast, 4-Cu lacks any fluorescence in this range – see Fig. S10.† When exciting the Q-band of 4-Mg and 4-Zn at 680 nm, fluorescence quantum yields of 0.19 and 0.2 with fluorescence lifetimes of 4.9 and 1.9 ns are determined using a zinc phthalocyanine as reference (0.3 and 3.1 ns in toluene)²⁶ (Fig. S11 and S12†).

To get further insights into the fluorescent behaviour of 5, the latter is excited at 520 nm and from the fluorescence at 550 nm a quantum yield of 0.69 and lifetime of 5.3 ns were determined. Similarly, for 6, which was excited at 560 nm, a fluorescence at 600 nm developed with a quantum yield of 0.54 and a lifetime of 3.7 ns.

Next, we turned to 1-Mg and 2-Mg, which were excited at 410 nm – see Fig. 4. The fluorescence from S2 of the porphyrazine is replaced with Bodipy-centered fluorescence at 550 and 600 nm, respectively. As such, we postulate an energy transfer in 1-Mg

Fig. 4 Room temperature fluorescence spectra in the visible region of **4-Mg** (red), **1-Mg** (blue), and **2-Mg** (dark cyan) measured in toluene with solutions that exhibit the same optical absorbance of 0.01 at a 410 nm excitation wavelength.

and **2-Mg** from the higher singlet excited states, S2 and higher, of the porphyrazines to either Bodipy. Corroboration for this hypothesis came from the excitation spectra of the fluorescence at 550 and 600 nm, respectively – see Fig. S15.† Here, the porphyrazine characteristics are discernable through the visible range. Nevertheless, the energetically lower lying S1 fluorescence of **1-Mg** and **2-Mg** evolved in the region around 700 nm.

Fig. S16† shows the fluorescence spectra of **5** and **1-Mg** upon photoexcitation at 520 nm. In the case of **1-Mg** the Bodipy-centered fluorescence is quenched by up to 93.6%, when compared to the model compound **5**, leading to a quantum yield of only 0.044. It is important to note that fluorescence evolves at 710 nm, which is assigned to the intrinsic fluorescence of the porphyrazine core. Here, an energy transfer takes place from Bodipy to porphyrazine with an efficiency of almost 0.8. This trend is also notable for **1-Cu** and **1-Zn**, as summarized in Table 2. By the same token, energy transfer occurs when exciting the Bodipy in **2-Mg** at 560 nm. For example, the fluorescence features a maximum at 600 nm, which is, however,

quenched by 92.9% when compared to **6** only – see Fig. 5. As a consequence, the overall quantum yields decrease from 0.54 to 0.038. Again, an additional characteristic fluorescence appeared in the Q-band range at 710 nm. This corroborates an energy transfer in **2-Mg** from the peripheral Bodipy to the porphyrazine core with a 25% efficiency. Additional details are derived from the time resolved emission spectra, which are displayed in Fig. S17–S21† and summarized in Table S2.†

Fluorescence quantum yields were determined as 0.06 (**1-Mg**) and 0.01 (**2-Mg**) upon excitation at 680 nm in each case. The fluorescence lifetimes are 5.2 and 5.7 ns for **1-Mg** and **2-Mg**, respectively. By the same token, quantum yields of 0.12 and 0.08 as well as lifetimes of 1.9 and 1.2 ns are established for **1-Zn** and **2-Zn**, respectively – Fig. S13.†

For the porphyrazines **1-Cu** and **2-Cu**, an energy transfer from the S2 to the corresponding Bodipy takes place and is depicted in Fig. S14,† but no fluorescence in the Q-band region is detected. To gain further insight into the fluorescence behaviour, fluorescence spectroscopy in the near-IR was performed, as illustrated in Fig. 6. In addition to the fine structure of the intrinsic fluorescence for **4-Mg** and **4-Zn**, weak spin-forbidden phosphorescence evolves for **4-Cu** with maxima at 1068, 1165, and 1228 nm.

Femtosecond transient absorption spectroscopy was used to obtain further insights into the excited state interactions in **1** and **2** and to corroborate the proposed energy transfer processes. To this end, **1**, **2**, **4**, **5**, and **6** were probed with 387, 530, and 695 nm excitation.

In the case of **4-Mg**, the singlet excited state – formed essentially right after the laser pulse – induces a net decrease of the absorptions at 506, 623, and 705 nm, regions which are dominated by strong **4-Mg** ground state absorptions – see Fig. 7. This suggests consumption of **4-Mg** as a result of converting its singlet ground state to the corresponding singlet excited state. An immediately formed absorption accompanies the transient bleaching. For example, the **4-Mg** based singlet excited state exhibits new absorption bands at 833 and 914 nm. The singlet transients produced upon 695 photoexcitation decay with

Fig. 5 Room temperature fluorescence spectra in the visible region of **6** (dark cyan), **2-Cu** (black), **2-Mg** (red), and **2-Zn** (grey) measured in toluene with solutions that exhibit the same optical absorbance of 0.01 at a 560 nm excitation wavelength.

Fig. 6 Normalized room temperature fluorescence spectra in the NIR region of **4-Cu** (black), **4-Mg** (red), and **4-Zn** (grey), in toluene with solutions that exhibit the same concentration (1×10^{-6} M) at a 685 nm excitation wavelength.

Fig. 7 Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (695 nm and 200 nJ) of **4-Mg** in toluene with several time delays between 0 and 8000 ps at room temperature. Insert – time-absorption profiles of the spectra at 710 and 900 nm, monitoring the intersystem crossing dynamics (*i.e.* 4.9 ± 0.4 ps).

lifetimes of 4.9 ± 0.4 ns *via* intersystem crossing to the corresponding triplet manifold. Similar behavior is observed when **4-Zn** and **4-Cu** – see Fig. S22 and S23† – are excited at 695 nm. In the case of **4-Zn** new absorption bands emerge at 535 and 910 nm, while the intersystem crossing to the triplet manifold features a lifetime of 1.6 ± 0.1 ns. Finally, for **4-Cu** new absorption features evolve at 430 and 900 nm, from which a short lifetime of 0.48 ± 0.08 ps is derived, followed by an intersystem crossing to the corresponding long lived triplet manifold.

The corresponding femtosecond experiments with **5** and **6** reveal the instantaneous formation of the singlet excited state features upon 530 nm laser excitation – see Fig. S24 and S25.† Here, the transient absorption spectra are dominated by strong bleaching between 450 and 650 nm for **5** and between 500 and 700 nm for **6**. The latter are due to the depletion of the singlet ground states and the concurring population of the singlet excited states. In the 400 to 500 nm and the 1000 to 1200 nm regions, additional maxima emerge. Overall, all of the aforementioned singlet excited state features are long-lived with lifetimes of 4.8 ± 0.2 (**5**) and 0.9 ± 0.1 ns (**6**) and implicate a slow intersystem crossing to the corresponding triplet manifolds.

The spectral features of **1-Mg** around 1 ps upon excitation at 530 nm are almost identical with those recorded for the singlet excited state of **5** – see Fig. 8. The lifetime of the latter is, however, impacted by the presence of the covalently attached porphyrazine. Formation of a new transient develops as a result of the rapid decay (*i.e.* 5.8 ± 0.2 ps) of the Bodipy singlet excited state. This, in fact, replaces in **1-Mg** the much slower intersystem crossing to the triplet excited state noted in **5**. Importantly, the new transient resembles the singlet excited state characteristics of **4-Mg**, that is, maxima at 428 and 914 nm as well as minima at 497, 632, and 705 nm. This suggests involvement of the singlet excited state of porphyrazine in an intramolecular energy transfer, as it occurs between the photoexcited Bodipy and the singlet ground state of the porphyrazine.

Fig. 8 Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm and 200 nJ) of **1-Mg** in toluene with several time delays between 0 and 8000 ps at room temperature. Insert – time-absorption profiles of the spectra at 520 and 710 nm, monitoring the intramolecular energy transfer dynamics (*i.e.* 5.8 ± 0.2 ps).

Likewise, upon exciting **2-Mg** at 530 nm, the Bodipy singlet excited state features are seen early on, namely after 1 ps – see Fig. 9. In line with the stronger photoreactivity of **2-Mg**, the Bodipy singlet excited state decays much faster with 5.5 ± 0.3 ps in the presence of the porphyrazine than in **1-Mg**. Importantly, maxima at 910 nm as well as minima at 497, 631, and 705 nm as they evolve simultaneously with the Bodipy singlet excited state decay are exact matches of the porphyrazine singlet excited state and, in turn, confirm the transduction of singlet excited state energy.

Turning to the 530 nm excitation of **1-Zn**, again the singlet excited state features of Bodipy are formed immediately after excitation and are accompanied by a strong ground state bleaching – see Fig. S26.† The latter then decays with 8.7 ± 1.4 ps. The transduction of singlet excited state energy was confirmed by detecting maxima at 900 nm as well as minima at 475, 635, and 705 nm, which are exact matches of what has been seen for the **4-Zn** singlet excited state. In **2-Zn**, a new transient

Fig. 9 Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm and 200 nJ) of **2-Mg** in toluene with several time delays between 0 and 8000 ps at room temperature. Insert – time-absorption profiles of the spectra at 590 and 710 nm, monitoring the intramolecular energy transfer dynamics (*i.e.* 5.5 ± 0.3 ps).

Fig. 10 Energy diagrams illustrating the intramolecular energy transfer processes of the different light harvesting Bodipy–porphyrazine conjugates.

develops as a result of the rapid decay (2.5 ± 0.2 ps) of the Bodipy singlet excited state, which replaces the much slower intersystem crossing to the triplet excited state – Fig. S27.† The newly formed transient resembles the singlet excited state characteristics of **4-Zn**, that is, maxima at 535 and 910 nm as well as minima at 475, 635, and 705 nm. Again, we hypothesize that an intramolecular energy transfer takes place between the photoexcited Bodipy and the porphyrazine in **2-Zn**.

Fig. S28† shows the differential absorption changes recorded upon 530 nm excitation of **1-Cu**. In **1-Cu**, the singlet excited state of Bodipy decays, however, rather slowly with a lifetime of 4.4 ± 0.5 ps. At the end of this process, maxima at 430 and 900 nm as well as minima at 495, 635, and 705 nm are noted. All of the aforementioned match those noted upon the photoexcitation of **4-Cu**. This is taken as evidence in support for the transduction of singlet excited state energy. On a longer time-scale, the fate of the porphyrazine-based singlet excited state is identical to what is seen for **4-Cu**. In this regard, a fast intersystem crossing, driven by a strong spin–orbit coupling, governs the rapid transformation of the singlet into the triplet excited state. Very similarly, in 530 nm excitation experiments with **2-Cu** the singlet excited state of Bodipy features evolve right after the conclusion of the excitation – see Fig. S29.† A new transient develops as a result of the rapid decay (*i.e.* 5.3 ± 0.3 ps) of the Bodipy-based singlet excited state. In fact, the latter replaces the intersystem crossing to the triplet excited state, in **2-Cu** with the singlet excited state characteristics seen for the reference, namely **4-Cu**. Notable here are maxima at 430 and 900 nm as well as minima at 495, 635, and 705 nm. The aforementioned corroborate that in **1-Cu** and **2-Cu** an energy transfer prevails between the Bodipys and the porphyrazine fragments.

In reference experiments, **4**, **5** and **6** were excited at 387 nm. However, due to the dominating absorptions of the porphyrazines at the 387 nm excitation wavelength, no appreciable Bodipy features were seen at any time following the excitation. Instead, only the porphyrazines characteristics emerge – *vide supra*.

Conclusions

A novel set of porphyrazines was designed, synthesized, and probed with respect to panchromatic light harvesting. On one hand, zinc, copper, or magnesium ions were complexed by porphyrazines to tune their ground and excited state features. On the other hand, up to eight Bodipys were covalently attached to the periphery of the porphyrazines to enhance the ground state absorption. As such, we realized broad absorption cross sections throughout most of the visible range and excited state energy funnelling in the corresponding star-shaped conjugates. Fig. 10 gives an illustrative example of the photophysical processes corroborated in measurements based on time-resolved fluorescence and femtosecond transient absorption spectroscopy. From the latter we derive the lack of ground state interactions, but strong intramolecular interactions in the excited state. Spectroscopic and kinetic evidence support a fast and unidirectional singlet excited state energy transfer from the photoexcited Bodipys at the periphery to the porphyrazines at the core upon visible light excitation from 450 to 650 nm. To this end, singlet excited state lifetimes of 8.7 and 5.8 ps for **1-Zn** and **1-Mg**, respectively, and 2.5 and 5.5 ps for **2-Zn** and **2-Mg**, respectively, were determined and reflect the exergonic energy transfer (~ 1.7 eV). From the aforementioned we established the following order of energy transfer rates **1-Zn** < **2-Mg** < **1-Mg** < **2-Zn**. A better spectral and orbital overlap between the Bodipys and the porphyrazines is a likely reason for this trend. Once the transduction of singlet excited state energy is concluded a porphyrazine-centered intersystem crossing to the corresponding triplet excited states evolves prior to the repopulation of the singlet ground state. This photoreactivity changes slightly, however, upon excitation in the 350 to 450 nm range. Notably, in this range higher lying singlet excited states of the porphyrazines are formed, which are the beginning of an energy transfer ping-pong, that is, from the higher lying singlet excited states of the porphyrazines (~ 2.8 eV) to the singlet excited states of Bodipys (~ 2.6 eV) and back to the porphyrazines (~ 1.7 eV), but to their singlet excited states. **1-Cu** and **2-Cu** react differently, owing to the fact that a heavy atom effect facilitates a fast intersystem crossing within a few hundredths of picoseconds. The impact of overlapping orbitals of Bodipy and metalloporphyrazine is clearly demonstrated, rendering the title compounds promising candidates in the design of panchromatic light harvesting systems for artificial photosynthesis by different combinations of antenna and basic chromophore moieties.

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